

What is claimed is:

1. A method of manufacturing a semiconductor device which is formed with a laminate metal film having a copper metal layer mainly containing copper and a barrier layer containing a metal more susceptible to oxidization than copper, said method comprising the steps of:
  - forming a barrier layer on the bottom and sides of a recess formed in an insulating film on a semiconductor substrate;
  - forming said copper metal layer such that said copper metal layer covers said barrier layer and fills in said recess;
  - removing an oxide formed on the surface of said copper metal layer due to exposure of the surface of said copper metal layer to oxygen with a solution including an organic acid having at least one carboxyl group; and
  - performing a heat treatment for growing grains of the copper.
2. The method of manufacturing a semiconductor device according to claim 1, wherein said organic acid is a compound which belongs to any of monocarboxylic acid, dicarboxylic acid, tricarboxylic acid, oxycarboxylic acid, and aminocarboxylic acid.
3. The method of manufacturing a semiconductor device according to claim 2, wherein said compound is oxalic acid.
4. The method of manufacturing a semiconductor device according to claim 1, wherein said heat treatment is performed in an inert atmosphere.

5. The method of manufacturing a semiconductor device according to claim 1, wherein said barrier layer is a metal layer including tantalum.

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6. The method of manufacturing a semiconductor device according to claim 1, wherein said laminate metal film is used as a wire or a via plug for connecting wires to each other.

10 7. A method of manufacturing a semiconductor device which is formed with a laminate metal film having a copper metal layer mainly containing copper and a barrier layer containing a metal more susceptible to oxidization than copper, said method comprising the steps of:

forming a barrier layer on the bottom and sides of a recess  
15 formed in an insulating film on a semiconductor substrate;

forming said copper metal layer such that said copper metal layer covers said barrier layer and fills in said recess;

polishing said laminate metal film until the top surface of said insulating film is exposed;

20 removing an oxide formed on the surface of said copper metal layer due to exposure of the surface of said copper metal layer to oxygen with a solution including an organic acid having at least one carboxyl group; and

performing a heat treatment for growing grains of the copper.

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8. The method of manufacturing a semiconductor device

according to claim 7, wherein said organic acid is a compound which belongs to any of monocarboxylic acid, dicarboxylic acid, tricarboxylic acid, oxycarboxylic acid, and aminocarboxylic acid.

5            9.     The method of manufacturing a semiconductor device according to claim 8, wherein said compound is oxalic acid.

             10.    The method of manufacturing a semiconductor device according to claim 7, wherein said heat treatment is performed in an inert  
10    atmosphere.

             11.    The method of manufacturing a semiconductor device according to claim 7, wherein said barrier layer is a metal layer including tantalum.

15           12.    The method of manufacturing a semiconductor device according to claim 7, wherein said laminate metal film is used as a wire or a via plug for connecting wires to each other.